PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : C08F 210/18 — A1

(11) International Publication Number: WO 88/ 04674

(43) International Publication Date: 30 June 1988 (30.06.88)

(21) International Application Number: PCT/US87/03299

(22) International Filing Date: 16 December 1987 (16.12.87)

(31) Priority Application Number: 944,381

(32) Priority Date: 19 December 1986 (19.12.86)

(33) Priority Country: US

(71) Applicant: EXXON CHEMICAL PATENTS, INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036-0710 (US).

(72) Inventors: WELBORN, Howard, Curtis, Jr. ; 1952 Vermont Avenue, Houston, TX 77019 (US). AUSTIN, Richard, Graham ; 4810 River Hill Drive, Kingwood, TX 77345 (US).

(74) Agent: HUNT, John, F.; Exxon Chemical Company, P.O. Box 5200, Baytown, TX 77522-5200 (US).

(81) Designated States: AU, BR, DK, FI, HU, JP, KR, NO.

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: UNSATURATED ETHYLENE POLYMERS

(57) Abstract

Ethylene alpha, internal nonconjugated diene unsaturated copolymers and higher interpolymers having structural characteristics that provide improved physical properties and processability. The ethylene polymers of the invention have narrow molecular weight distribution and/or narrow composition distribution and/or a low cluster index. Ethylene/1,4-hexadiene and ethylene/vinyl cyclohexene polymers have residual unsaturation for subsequent modifications and for applications with improved toughness, printability, melt processability, and other advantageous characteristics.

2008年 5月29日 18時45分 発信国際特許庁 NO. 5624 P. 22

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SN	Senegal
CH	Switzerland	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
DE	Germany, Federal Republic of	LU	Luxembourg	TG	Togo
DK	Denmark	MC	Monaco	US	United States of America
FI	Finland	MG	Madagascar		

2008年 5月29日 18時45分 特許庁審査第一部 NO. 5624 P. 23

UNSATURATED ETHYLENE POLYMERS

BACKGROUND OF THE INVENTION

This invention relates to unsaturated ethylene polymers in general and in particular to such polymers having residual unsaturation, and formed by the polymerization of ethylene and an alpha, internal nonconjugated diene (diolefin) comonomer. Optionally, other monomers are also incorporated in the polyethylene structure.

Polymers consisting primarily of ethylene monomer are widely recognized materials for a great variety of uses in many fields. Certain other polymers have disadvantages for some applications because of the physical properties associated with the polymer structure, whether from the incorporation of a comonomer or from the method of polymerization of the polymer. Most homopolymers and copolymers of alpha-olefins are widely used because of their inexpensive nature and excellent physical properties including transparency, moldability, chemical resistance, and other aspects. However, such polymers generally do not have widespread suitability for other substrates, surfaces, and materials due to their non-polar structure. Accordingly, most such homopolymers, copolymers, and higher interpolymers are not generally suitable for coatings, printing, and antistatic applications. Various methods and treatments have been devised to overcome the general shortcoming of such polymers. These include treating the polymers with oxidizing agents, degrading agents, and the like, but such measures have not always proven satisfactory for all applications.

The present invention is related to ethylene homopolymers, copolymers, terpolymers, and higher interpolymers of ethylene and other copolymerizable comonomers which have alpha, internal nonconjugated unsaturation. Such polymers always include a comonomer moiety which provides unsaturation in the polymer, the unsaturation being for subsequent modification or use in the various applications for which the ethylene polymers are not otherwise suitable. Polymers of ethylene are needed which not only incorporate residual unsaturation but also have outstanding physical properties above those commonly found in the predecessors of the present invention.

2008年 5月29日 18時45分 発信者情報 NO. 5624 P. 24

Ethylene and other alpha-olefins are traditionally polymerized or copolymerized in the presence of catalytic complexes formed from mixtures of transition metal compounds and aluminum alkyls. Such complexes necessarily produce polymers and interpolymers which have physical properties depending on the catalyst and method of polymerization.

Prior art polymers have suffered from one or more difficulties affecting their physical properties, especially for the residual unsaturation polymers to which the present invention is related since these polymers may not often be modified or degraded without affecting the residual unsaturation content. The difficulties include broadened molecular weight distributions, broadened composition distribution of comonomer, and inefficient distribution or dispersion of the comonomer along the polyethylene chain of the copolymer. Of course, it is recognized that the polymers of the invention have residual unsaturation along the side chains substituted on the main polyethylene chain of the invention.

Broadened molecular weight distribution of a polymer strongly influences its melt flow properties and such polymers tend to have a high concentration of high molecular weight molecules making them subject to orientation. As a result, such resins produce strongly anisotropic physical properties in the machine transverse direction of a fabrication process and such properties are detrimental to a number of end use applications.

Broad molecular weight distribution resins also frequently contain a significant portion of quite low molecular weight material. These molecules almost invariably contain high concentrations of comonomer and therefore tend to be amorphous or of a low degree of crystallinity. Consequently, these materials exude to the surface of fabricated parts causing tackiness where not desired and/or interfere with other additives in the polymer designed according to the particular application. An example of this is the surface active property associated with slip agents in blown or cast film.

Most prior art copolymers tend to have a very broad composition distribution of comonomer, i.e., the distribution of comonomer among the polymer molecules being nonuniform, some

molecules having a relatively high concentration of comonomer while others have a relatively low concentration of comonomer. This structural property of the prior art polymers allows that portion with low comonomer content to have a high melting point and vice versa leading to a broad melting range for the entire polymer composition. Of course the presence of a high melting component is disadvantageous for many applications where softness is desired and may lead to undesired stiffness. On the other hand, the presence of high comonomer content materials of low melting point frequently results in a high quantity of extractables.

Prior art materials are generally characterized by relatively inefficient use of comonomer moieties along the polyethylene chains. The distribution of the comonomer along the chain is very important in determining the efficiency of use of the comonomer and the resulting properties of the polymer, especially with respect to crystallizability of the polymer. Such prior art polymers tend to have a high degree of clustering of the comonomer moieties along the polyethylene chain. That is, the comonomer units are adjacent or nonisolated along the chain resulting in inefficient use of the comonomer since only a single polyethylene chain interruption results when several comonomer units are contiguous. This has extremely important implications in the total amount of comonomer required to achieve the desired crystallinity. Also, it is often disadvantageous to include unneeded portions of comonomer, especially when dealing with less available and more expensive diene comonomers. Frequently, the requirement to use a higher portion of comonomer also tends to force the comonomer into low molecular weight, high comonomer content ends of the molecular weight distribution. Accordingly, improved unsaturated ethylene copolymers, terpolymers, and interpolymers in the entire range of amorphous to highly crystalline polymers is needed.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graphic and verbal depiction of the concept of cluster index;

Figure 2 is a plot of cluster index against mole percent comonomer for several commercial resins and the unsaturated resin of the invention;

Figure 3 is an overlay of a plot of the molecular weight distribution of resin of the invention over that for commercial resin 3, plotted against weight percent comonomer content;

Figure 4 is a series of plots of comonomer distribution in weight percent versus elution temperature for resin of the invention and several commercial resins;

Figure 5 is a plot evidencing the correlation of elution temperature and polymer composition in branches/1000 carbon atoms (mole percent comonomer);

Figure 6 is a plot for comparison to Figure 6A, showing the relative breadth of melting point for some commercial polymers;

Figure 6A is a plot of the melting point by DSC for three copolymers of the invention (Examples 1- 2A).

SUMMARY OF THE INVENTION

The present invention is directed to providing polymers of ethylene and at least one comonomer wherein the at least one comonomer is an alpha, internal nonconjugated diolefin and wherein the polymer has excellent physical properties resulting from the structure of the polymer and also has residual unsaturation. The polymers of the invention generally comprise at least about 50 percent ethylene and the remainder alpha, internal nonconjugated diolefin and optionally other polymerizable comonomer content. When used herein, the term copolymer is intended to include terpolymers and higher interpolymers of ethylene as well as the simple copolymer of ethylene with a single diolefin or mixture of such alpha, internal nonconjugated diolefins. Therefore, the term copolymer includes terpolymers and interpolymers when referring to the polymers of the present invention.

The polymers of the present invention may have a broad range of densities and, therefore, applications for the particular type of copolymer. In addition, the residual unsaturation of the copolymer may vary quite widely by design according to the invention so as to provide a copolymer of particular suitability for certain applications. The polymers may be liquid or solid.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A copolymer composition from the polymerization of ethylene and at least one polymerizable comonomer comprising an alpha,

2008年5月29日 18時46分 発信国特許庁 NO. 5624 P. 27

internal nonconjugated diene, said copolymer having a composition distribution wherein at least about 55 weight percent, preferably about 65 weight percent, more preferably about 70 weight percent of the copolymer molecules have a comonomer content within about 50 percent of the median comonomer content in mole percent of said copolymer composition.

By way of explanation, a copolymer having a median (equal amount greater and less than) comonomer content of 2.0 mole percent would have 55 weight percent, preferably 65, more preferably 70 weight percent of its composition with a comonomer content of 1.0 to 3.0 mole percent.

Another preferred embodiment of the present invention is a copolymer composition from the polymerization of ethylene and at least one polymerizable comonomer comprising an alpha, internal nonconjugated diene, said copolymer having a molecular weight distribution (Mw/Mn) of about 3.0 or less, preferably 2.5 or less, preferably about 2.0.

Another preferred embodiment of the present invention is a copolymer composition from the polymerization of ethylene and at least one comonomer comprising an alpha, internal nonconjugated diene, said copolymer composition having incorporated in its structure at least 3 mole percent preferably 5 mole percent, more preferably 10 mole percent of units of said at least one comonomer, said copolymer composition having a cluster index of about 9 or less, preferably between 5 and 0.

The ethylene copolymers of the invention have improved properties resulting especially from the more efficient use of diene comonomer in controlling the crystallizability of the polymer. That is, the efficient use of the diene comonomer comprises an improved isolation of the comonomer molecules along the polyethylene chain as not previously achieved for ethylene copolymers having residual unsaturation. Accordingly, the polymers of the present invention not only have especially good application for those uses previously employing residual unsaturation polymers, but also have excellent overall physical properties marking a significant improvement over those materials previously available. The improved properties of the invention result from the isolated dispersion of the diene comonomer

2008年 5月29日 18時47分 特許庁審査官 NO. 5624 P. 28

and other comonomers along the sequence of the polymer molecule of the invention.

Another preferred embodiment copolymer of the present invention has a distribution wherein more than 55 weight percent of the copolymer molecules are within 50 percent of the median comonomer content in the mole percent, said copolymer being formed by polymerization in the presence of a catalyst system comprising a metallocene of a metal of Group IVB, VB, and VIB of the Periodic Table and an alumoxane or reaction product thereof.

The unsaturated copolymer products of the present invention comprise batchwise or continuously produced bulk polymer compositions having the properties and characteristics described herein. No such compositions have heretofore been discovered. That is, the entire/unmodified polymerization product has the advantageous properties.

The unsaturated copolymer compositions of the invention may be prepared from the polymerization of ethylene and at least one comonomer. The at least one comonomer comprises, that is always includes some (or all) of the alpha, internal nonconjugated diene.

The alpha, internal nonconjugated diene comonomers of the invention may be linear or cyclic, branched or unbranched, short or long chained.

The diene comonomers incorporated in the unsaturated polymers of the invention may be in small or large quantity relative to the amount of ethylene in the polymer. In one embodiment of the invention, the polymers of the invention contain at least a minimum of about 3 mole percent total comonomer based on the moles of ethylene and comonomers, so as to provide wide dispersion of the comonomers in the polymer product composition. This generally limits the density to a number below 0.930 g/cc, preferably below 0.920 g/cc depending on the copolymers chosen and the method of incorporation. Thus, where only a two component polymer composition is formed from ethylene and the alpha, internal nonconjugated diene, at least about 3 mole percent diene units and no more than about 97 mole percent ethylene units are present. For terpolymers and higher interpolymers of the invention, only about 0.01 mole percent or more, preferably about 0.1 mole percent or more, more preferably 1 mole percent or

more of the diene need be incorporated so long as the total incorporation of comonomers (diene and other[s]) is at least about 3 mole percent for this embodiment.

Despite incorporation of at least about 3 mole percent comonomer units in one embodiment of the polymer compositions of the invention the polymers nevertheless have a low cluster index and preferably other characteristics described herein. The total comonomer content of the polymers of the invention may be the predominant portion of the polymer. Preferably, especially for solid unsaturated polymers, the ethylene units are the predominant component on a molar basis.

In one preferred embodiment of the present invention the polymers of the invention have improved properties attributable to the more uniform content of diene and other comonomer among the polymer molecules.

In contrast to the prior art polymers, the copolymers, terpolymers, and other interpolymers of the present invention have residual unsaturation and exhibit very little clustering of the comonomer molecules along the polyethylene chain both with respect to the diene comonomer and any other polymerizable comonomer formed in the polyethylene chain. As a result, the use of comonomer in forming the copolymers of the invention is very efficient in controlling crystallizability, wards against formation of high comonomer content/low molecular weight ends, reduces cost, and improves properties.

In a preferred embodiment of the present invention, the copolymers of the invention have very narrow composition distribution of comonomer. That is, the copolymers have much more uniform distribution of comonomer among the molecules thereby largely avoiding the problem presented by broad composition distribution resins.

In another preferred delineation of the invention, the copolymers of the invention have improved properties resulting from the more consistent size of polymer molecules not achieved in the prior art. This aspect of the more preferred embodiment is generally referred to as the improved molecular weight distribution or ratio of the weight average molecular weight to number average molecular

2008年5月29日 18時47分 翻訳特訳 NO. 5624 P. 30

weight of the polymer material.

Also in this preferred embodiment of the present invention, the copolymers of the invention exhibit relatively narrow molecular weight distribution. That is, they have a relatively low ratio of weight to number average molecular weight. In other words, the concentration of very high molecular weight molecules and very low molecular weight molecules is decreased over prior art unsaturated polymers. The absence of the high molecular weight molecules reduces the tendency for orientation in fabrication processes and increases isotropic machine/transverse direction physical properties. The absence of a low molecular weight molecules (low tail) in the copolymers of the invention reduces the tendency to form tacky surfaces and otherwise interfere with surface active agents in certain applications of the copolymers of the present invention.

Unsaturated polymers of the prior art do not have the structure and corresponding properties of the polymers of the invention. That is, they lack the low cluster index for ethylene copolymers (including terpolymers and higher interpolymers) having therein at least about 3 mole percent, preferably 5 mole percent, more preferably 10 mole percent comonomer units according to the invention. The absence of such structure is generally reflected in easily measured characteristics of the invention such as melting point temperature and the like. The prior art unsaturated polymers also generally lack narrow molecular weight distribution and narrow comonomer distribution.

The polymers of the present invention are capable of being fabricated into a wide variety of articles, as is known for homopolymers of ethylene and copolymers of ethylene and higher alpha-olefins. Furthermore, the polymers of the present invention typically have residual unsaturation which permits their use in additional applications where the residual unsaturation may be used for bondability, printability, crosslinkability, and the like.

The unsaturated polymers of the invention may vary in density across a broad scale from essentially amorphous materials to highly crystalline materials. They may be liquids (such as for certain rubbers and lubricants and waxes) or solids.

The molecular weight of the copolymers of the invention may

2008年5月29日 18時48分 特許審査第一部 NO. 5624 P. 31

vary over a broad range. Preferably the polymers have a number average molecular weight of about 500 or higher, preferably 1000 or higher, more preferably about 10,000 or higher. Typically, materials used for elastomers applications are either copolymers or terpolymers (often with propylene monomer) in the density range of about 0.86-0.87 g/cc. Typically, these polymers contain 30 weight percent or more of the comonomers and the balance ethylene. Frequently, the elastomers of the unsaturated polymers of the invention will have as much as 48 weight percent of the comonomer present.

The unsaturated polymers of the present invention may also include plastomers in the density range of about 0.87-0.900 g/cc and containing from about 20-30 weight percent of comonomer. Also available in the unsaturated polymers of the invention are the very low density polyethylene materials of density range 0.900-0.915 g/cc and having from about 10-20 weight percent comonomer present.

The unsaturated polymers of the invention may be formed as a linear low density polyethylene type polymer in the density range of about 0.915 g/cc to about 0.940 g/cc and containing from about 5-10 weight percent of the comonomers. The unsaturated polymers of the invention may also be used in the form of high density polyethylene having a density of about 0.940 g/cc and above and containing up to about 5 weight percent comonomers. The unsaturated polymers of the invention may also form amorphous materials below a density of 0.86 g/cc including tackifier resins.

The unsaturated polymers of the present invention have particularly advantageous properties because of their narrow molecular weight distribution, narrow compositional distribution, and their chain configuration having isolated comonomer units.

Sequence distributions, or the distribution of comonomer units along a polymer chain, in, e.g., linear low density polyethylenes is a factor affecting the cost of the polymer because it affects the amount of comonomer required to achieve a desired polymer density. If comonomer is efficiently incorporated, i.e., with little clustering of comonomer units, in a linear low density polyethylene, less comonomer is required to depress the density. Thus, the number of comonomer runs in a copolymer chain and the length of each run is significant in the structure of the

2008年 5月29日 18時48分 特許庁審査第一部 NO. 5624 P. 32

polyethylene molecules and affects the physical properties of the polymer. The polymers of the present invention are marked by a relatively high number of single units of comonomer in the polymer chain relative to the number of units containing more than a single comonomer molecule in comparison to unsaturated polymers of the prior art.

The unsaturated ethylene polymers of the invention are hereinafter described by their "cluster index". This index reflects the degree to which the polymers of the invention have individual comonomer units dispersed along the polyethylene chain, preferably in favoring isolation of individual units over groups of two or more units. Given a minimum level of comonomer, the unsaturated ethylene polymers of the present invention are especially noted for their efficient use of comonomer molecules by having more isolated comonomer molecules along the polyethylene chain and fewer clusters of molecules of the comonomer in the polyethylene chain. That is, the unsaturated polymers of the present invention tend to deviate from random comonomer distribution in the direction of fewer contiguous comonomer sequences. Thus, the cluster index permits a quantitative evaluation of the deviation from a random distribution of comonomer in the polymer chain.

In the cluster index description given herein, there are two reference points. The reference point 0 describes a polymer which has only isolated comonomer insertions without any contiguous comonomer units in a cluster; of course this describes pure homopolymers also. The second reference point is the number 10 describing an ethylene copolymer having comonomer distribution that is exactly random (Bernoullian) and thus containing a predictable amount of contiguous comonomer units. Any polymer having a cluster index value greater than 10 contains proportionally more contiguous comonomer sequences than predicted by the random distribution. Any polymer having a cluster index value between 0 and 10 is indicated to have fewer contiguous sequences than a random distribution polymer (given a minimum of comonomer). These values are typically associated with the method of producing the polymer including the catalyst used and conditions of polymerization.

The cluster index comparisons are best made for polymers

having comparable comonomer mole contents or densities. The measurement of the clustering of the comonomer along the polyethylene chain in a given polymer may be determined by a study using carbon 13 nuclear magnetic resonance spectroscopy (C^{13} NMR). Using this tool for evaluation, the cluster index may be given as follows:

$$\text{Cluster index} = 10\ [(X) - (EXE)]/[2(X)^2 - (X)^3]$$

where (X) is the mole % of total comonomer molecules in the copolymer and (EXE) is the mole fraction of the triad segment of 3 monomer units containing ethylene-comonomer-ethylene. These concentrations are easily measured using C^{13} NMR.

The basis for the cluster index is further explained and exemplified below by the following discussion and in reference to drawing Figure 1.

Referring now to drawing Figure 1 the cluster index may be derived as follows, using the reference point 10 as random clustering expected in a polymerization and the reference point 0 as that point for no clustering in a polymer (no units of more than one comonomer molecule contiguous). Accordingly,

$$\text{Cluster index} = 10 - 10 \times \frac{[(EXE)_{observed} - (EXE)_{random}]}{[(X) - (EXE)_{random}]}$$

where "X" is the mole % comonomer in the ethylene copolymer and EXE is the corresponding triad configuration of a single comonomer molecule contiguous to two ethylene molecules (units).

The term $(EXE)_{random}$ serves as a reference point and its value can be calculated from any suitable statistical model. In this case the Bernoullian model was chosen. For the Bernoullian model

$$(EXE)_{random} = [1 - X]^2[X].$$

Thus, substituting this value of $(EXE)_{random}$ in the formula for cluster index above gives:

$$\text{Cluster index} = 10\,[(X) - (EXE)_{observed}]/[2(X)^2 - (X)^3]$$

Accordingly, it can be readily seen from drawing Figure 1 that those polymers having more comonomer clustering than a random distribution appear to the left of the reference point 10 and those having less comonomer clustering than a random distribution appear between 0 and 10.

In Figure 2, polymers are plotted according to their cluster index as described for Figure 1 and using the vertical axis to plot mole percent of comonomer of the polymer samples. It is readily apparent from drawing Figure 2 that those polymers of the invention have a reduced cluster index (for a given density) over polymers of the prior art such as those commercial polymers plotted and appearing near or to the left of reference point 10 (random clustering). The technique of using the C^{13} NMR to obtain the information for cluster index is known to the skilled artisan.

Also shown for comparison in Figure 2 is the cluster index of Dowlex 2088 octene LLDPE copolymer (Resin 9), Dowlex 2517 octene LLDPE copolymer (Resin 10), and Union Carbide 7099 hexene LLDPE copolymer (Resin 11).

The cluster index improvement in the polymers of the invention versus polymers of the prior art is detectable at 3 mole percent comonomer content, readily discernable at 5 mole percent, and remarkable at about 10 mole percent or higher.

The above described cluster index may be considered to be of the first order or based on the total number of comonomer units less the isolated (EXE) comonomer units. A higher order cluster index can also be measured and calculated as based primarily on the occurrence of dimer segments (EXX) or (XXE) as observed. This measurement is somewhat more discriminating at low comonomer mole percents (about 3). Thus, an EXX index may in like fashion be calculated as:

$$\text{EXX index} = 10 - 10 \times \frac{[(EXX)_{observed} - (EXX)_{Bernoullian}]}{(EXX)_{Bernoullian}}$$

Since $(EXX)_{Bernoullian} = 2[E][X]^2$ and the (EXX) observed is based on both (EXX) and (XXE) units, readily measured by C^{13} NMR, the EXX index is readily achieved. For such index a totally random polymer is measured as 10, a totally dimerless polymer is 0 (no contiguous XX), and a polymer increasingly deficient in solitary units (EXE) will approach 20.

The EXX index is a second measure of polymer structure based directly on dimers and higher orders of contiguous X (EXX and XXE) observed; it may be used independently or together with the cluster index (EXE) to distinguish polymers.

The EXX index for commercial resins 3, 5, and 6 in the Table herein are 7.3, 12.4, and 15.0. Compare the terpolymer resin of Example 2 of the invention which at 3.9 mole percent comonomer has an EXX index of only 8.2.

The unsaturated ethylene polymers of the present invention are preferably marked by a relatively narrow molecular weight distribution in comparison to prior art polymers. The molecular weights and molecular weight distributions were determined using Waters 150C Gel Permeation Chromatograhic Instruments. These instruments were equipped with refractive index detectors operated at 145°C and at a solvent flow rate of 1 milliliter per minute. The solvent used was ultra-high purity grade 1,2,4-trichlorobenzene obtained from Burdick and Jackson Company. Prior to use, the solvent was filtered through a 0.5 micron filter and stabilized with 120 ppm BHT. Three Waters styragel columns were used with nominal porosities of 500, 10,000, and 1,000,000 angstroms. Each polymer sample was dissolved in trichlorobenzene solvent at 145°C to a concentration level of about 0.1 weight percent and thereafter filtered through a 0.5 micron porous metal filter. About 300 microliters of this solution was then injected into the gel permeation chromatograph. Analysis time was typically 45 minutes. Calibration of the instrument for molecular weight determination was accomplished with the use of narrow molecular weight distribution polystyrene standards obtained from Toyo Soda Manufacturing Company. Sixteen of the standards were used ranging in molecular weight from 526 - 5.2×10^6. Molecular weight distributions of these standards were listed at 1.0-1.15 as measured by the ratio of weight average molecular

2008年 5月29日 18時49分 特許庁審査官 NO. 5624 P. 36

weight to number average molecular weight. These polystyrene molecular weight data were then converted to a polyethylene basis with the use of the Mark-Houwink equation and the use of the following constants:

for polyethylene $K = 5.17 \times 10^{-4}$, $a = 0.70$

for polystyrene $K = 2.78 \times 10^{-4}$, $a = 0.70$.

Each sample was run twice and the calculated results average to yield the molecular weight information reported. The molecular weight distribution of the resin of Example 1 below was plotted for comparison on the same plot with that for Exxon LL3001 linear low density polyethylene resin mole percent comonomer on a scale of the log of molecular weight versus weight percent of the polymer in the molecular weight range. As can be seen from drawing Figure 3 the unsaturated polymer of the invention has a strictly narrower molecular weight distribution than the commercially available linear low density polyethylene.

The unsaturated polymers of the present invention preferably also have a narrow distribution of comonomer amongst molecules of the polymer in comparison to prior art polymers. For comparison, drawing Figure 4 reflects the narrow distribution of the unsaturated polymer of Example 1 in comparison to the relatively broad comonomer distribution polymers of the prior art. In Figure 4 the weight percent of copolymer (having a given comonomer content) is plotted against an elution temperature which directly reflects comonomer content. A better understanding of this preferred embodiment of the polymers of the present invention will be had by a review of Figure 4 and the following discussion.

Crystalline copolymers may be fractionated by comonomer content over a temperature range from 0-120°C in tetrachloroethylene solvent. The compositions of the fractions of the copolymer are determined and a solution temperature versus composition calibration curve has been constructed based on the data obtained. Using this calibration curve, the temperature scale of the solubility distribution curve can be converted to a composition scale and a composition distribution curve is thus obtained as in drawing Figure 4.

A machine has been assembled to automatically determine the

solubility distribution curve of a crystalline copolymer. In the measuring instrument, a steel column is packed with small mesh glass beads and immersed in an oil bath whose temperature can be programmed over a temperature range from about 0°C-150°C. The tetrachloroethylene solvent may be prevented from boiling by operating the instrument at about 3 atmospheres pressure under an automatic regulator. A weighed amount of sample, usually about 1.6 grams, is placed in a sample preparation chamber, sealed, and repeatedly evacuated and filled with argon. A metered volume of solvent is then pumped into the sample preparation chamber where it is stirred and heated to obtain a solution of about 1 percent concentration. A metered volume of this solution, usually about 100 cc is then pumped into the packed column which has been thermostated at a high temperature of usually at least about 120°C.

The polymer solution sample is subsequently crystallized by cooling the polymer in the column to 0°C at a programmed rate of 5°C per hour. The column was then maintained at 0°C for at least an hour. Thereafter, the elution stage of the determination is started by pumping pure solvent through the column at a rate of 6 cc per minute. Effluent from the column passes through the reheater where it is heated to 120°C before passing through an IR detector used to measure the absorbance of the effluent stream. The infrared absorbents of the polymer carbon hydrogen stretching bands at about 2960 centimeter^{-1} serves as a continuous measure of the relative concentration of polymer in the effluent. After passing through the infrared detector the temperature of the effluent is reduced to about 110°C and the pressure is reduced to 1 atmosphere before passing the stream into an automatic fraction collector. In the elution stage, the pure solvent is pumped through the column set at 0°C for one hour. This serves to flush polymer that has not crystallized during the crystallization stage out of the column so that the percent of uncrystallized polymer can be determined from the infrared trace. The temperature is then programmed upward at 10°C per hour to 100°C and at 20°C per hour from 100°C to 120°C.

The compositions of fractions obtained from the various polymers were determined by infrared spectroscopy. The IR compositions are obtained from the intensity of the 1378(cm)$^{-1}$

2008年 5月29日 18時50分 特許庁審査官 NO. 5624 P. 38

methyl band, the thickness of the sample, and a calibration curve based on samples whose compositions were determined independently by C^{13} NMR. No corrections for polymer end groups was made in obtaining compositions from infrared data.

Figure 5 is a plot of the elution temperature versus the comonomer content in mole percent comonomer (branches per 1000 carbon atoms) for the fractions of the sample. The curve "A" has been drawn through the points. Thus, curve A may be used as a correlation between elution temperature and composition of the polymer for temperatures greater than 0°C. The calibration curve is most accurate for fractions with number average molecular weights, $M_n \geq 10,000$ as determined by size exclusion chromatography.

As seen in drawing Figure 4, samples of polymers tend to have a peak at about 0°C elution temperature. This small peak represents the fraction of total polymer that is not crystallizable at the lowest temperature of the experiment (about 0°C).

In summary, the device and procedure described provide a plot of relative weight percent of polymer versus elution temperature which in turn may be correlated to composition and mole percent comonomer (branches per 1000 carbon atoms) in the polymer chain. Accordingly, drawing Figure 4 is an effective comparison of the comonomer distribution of the unsaturated polymers of the invention to that for certain commercial polymers. As can readily be seen, the composition distribution of the polymer of the invention example is quite narrow in comparison.

The alpha internal nonconjugated dienes which form units of the copolymers (including terpolymers and higher interpolymers) of the invention include a variety of such diolefins exemplified by but not limited to the following:

1,4-hexadiene; 1,4-heptadiene; 1,5-heptadiene; 1,4-octadiene; 1,5-octadiene; 1,6-octadiene; 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 4-ethyl-1,4-hexadiene, 5-methyl-1,4-heptadiene; 5-ethyl-1,6-octadiene; 3-vinyl cyclohexene; 4-vinyl cyclohexene; 3-vinyl cyclopentene; cis and trans 1,5,9-decatriene; 5-vinyl norbornene; 1,4-dodecadiene.

Comonomers other than the dienes of the invention include polymerizable comonomers such as acids, esters, other olefins, and

2008年5月29日 18時50分 特許庁審査第一部 NO. 5624 P. 39

the like. Suitable olefins include the alpha olefins such as propylene, butene, hexene, octene, 4-methyl-pentene-1, and others.

According to the invention, the alpha-olefin content of the unsaturated ethylene polymers (copolymers) of the invention is less than 15 weight percent, preferably less than 10 weight percent.

In forming the polymers of the present invention it may be necessary to purify, or isolate the diene and other, optional comonomers of the invention in order to obtain incorporation thereof during polymerization. One such recommended technique is passing the comonomer, especially the diene, over alumina to remove extraneous materials.

Figures 6 and 6A show the melting point by differential scanning calorimetry results for the resins of the invention in comparison to some commercial resins. Melting point distributions were determined using a Perkin Elmer DSC-7 operated in the following fashion: About 5-6 mg of sample was heated to 160°C and held at that temperature for 5 minutes. The sample was then cooled at 10°C per minute to a temperature of 0°C and reheated at 10°C per minute. The melting distributions reported here were collected during this reheating at 10°C per minute.

Concentrations of unsaturation in ethylene based polymers was determined by comparisons of IR spectra of brominated versus original polymer specimens utilizing the following bands:

vinylene - 965 cm^{-1}

vinyl - 909 cm^{-1}

vinylidene - 888 cm^{-1}

A better understanding of the invention will be had by a review of the above discussion in conjunction with the drawing Figures and the Examples given below. The best mode of the invention presently known is described herein.

The unsaturated polymers of the present invention are those having the narrow cluster index and preferably having the additional described structure of molecular weight distribution and comonomer distribution as well as properties herein described. Such polymers may be prepared by any of the known techniques of polymerization including solution, high pressure, and gas-phase polymerization processes.

The polymers of the invention may be formed by use of catalyst systems of the metallocene type. That is,

2008年 5月29日 18時51分 欧州国際特許庁 NO. 5624 P. 40

cyclopentadienylide catalyst systems using a metallocene complex in conjunction with an alumoxane cocatalyst or reaction product thereof are suitable for preparing polymers of the invention. The metallocene catalyst may be represented by the general formula $(Cp)_mMR_nR'_p$ wherein Cp is a substituted or unsubstituted cyclopentadienyl ring; M is a Group IVB, VB, or VIB transition metal; R and R' are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms; m = 1-3, n = 0-3, p = 0-3; and the sum of m + n + p equals the oxidation state of M. Various forms of the catalyst system of the metallocene type may be used for polymerization to achieve polymers of the present invention including those of the homogeneous or the heterogeneous, supported catalyst type wherein the catalyst and alumoxane cocatalyst are together supported or reacted together onto an inert support for polymerization by gas-phase, high pressure, or solution polymerization.

The cyclopentadienyls of the catalyst may be unsubstituted or substituted with hydrogen or hydrocarbyl radicals. The hydrocarbyl radicals may include alkyl, alkenyl, aryl, alkylaryl, arylalkyl, and like radicals containing from about 1-20 carbon atoms or 2 carbon atoms joined together to form a C_4-C_6 ring. Exemplary hydrocarbyl radicals include methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like. Exemplary halogen substituents include chlorine, bromine, flourine and iodine and of these halogen atoms, chlorine is preferred. Exemplary hydrocarboxy radicals are methoxy, ethoxy, propoxy, butoxy, amyloxy and the like. Illustrative, but non-limiting examples of the metallocene catalyst useful in preparing the polymers of the present invention include bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diphenyl, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium dimethyl and diphenyl, bis(cyclopentadienyl)titanium di-neopentyl, bis(cyclopentadienyl)zirconium di-neopentyl, bis(cyclopentadienyl)titanium dibenzyl, bis(cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)vanadium dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)titanium methyl chloride,

bis(cyclopentadienyl)titanium ethyl chloride, bis(cyclopentadienyl)titanium phenyl chloride, bis(cyclopentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis(cyclopentadienyl)titanium methyl bromide, bis(cyclopentadienyl)methyl iodide, bis(cyclopentadienyl)titanium ethyl bromide, bis(cyclopentadienyl)titanium ethyl iodide, bis(cyclopentadienyl)titanium phenyl bromide, bis(cyclopentadienyl)titanium phenyl iodide, bis(cyclopentadienyl)zirconium methyl bromide, bis(cyclopentadienyl)zirconium methyl iodide, bis(cyclopentadienyl)zirconium ethyl bromide, bis(cyclopentadienyl)zirconium ethyl iodide, bis(cyclopentadienyl)zirconium phenyl bromide, bis(cyclopentadienyl)zirconium phenyl iodide; the trialkyl metallocenes such as cyclopentadienyltitanium trimethyl, cyclopentadienyl zirconium triphenyl, and cyclopentadienyl zirconium trineopentyl, cyclopentadienylzirconium trimethyl, cyclopentadienylhafnium triphenyl, cyclopentadienylhafnium trineopentyl, and cyclopentadienylhafnium trimethyl.

Other metallocenes which may be usefully employed to prepare the polymers of the invention include the monocyclopentadienyls titanocenes such as, pentamethylcyclopentadienyl titanium trichloride, pentaethylcyclopentadienyl titanium trichloride; bis(pentamethylcyclopentadienyl) titanium diphenyl, the carbene represented by the formula bis(cyclopentadienyl)titanium=CH_2 and derivatives of this reagent such as bis(cyclopentadienyl)$Ti{=}CH_2.Al(CH_3)_3$, $(Cp_2TiCH_2)_2$, $Cp_2\overline{TiCH_2CH(CH_3)CH_2}$, $Cp_2\overline{Ti-CHCH_2CH_2}$; substituted bis(cyclopentadienyl)titanium (IV) compounds such as: bis(indenyl)titanium diphenyl or dichloride, bis(methylcyclopentadienyl)titanium diphenyl or dihalides; dialkyl, trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds such as bis(1,2-dimethylcyclopentadienyl)titanium diphenyl or dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or dichloride and other dihalide complexes; silicon, phosphine, amine or

2008年5月29日 18時51分 国際調査報告 NO. 5624 P. 42

carbon bridged cyclopentadiene complexes, such as dimethyl silyldicyclopentadienyl titanium diphenyl or dichloride, methyl phosphine dicyclopentadienyl titanium diphenyl or dichloride, methylenedicyclopentadienyl titanium diphenyl or dichloride and other dihalide complexes and the like.

Additional zirconocene catalysts useful according to the present invention include bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)zirconium methylchloride, pentamethylcyclopentadienyl zirconium trichloride, pentaethylcyclopentadienyl zirconium trichloride, bis(pentamethylcyclopentadienyl)zirconium diphenyl, the alkyl substituted cyclopentadienes, such as bis(ethyl cyclopentadienyl)zirconium dimethyl, bis(β-phenylpropylcyclopentadienyl)zirconium dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl, bis(n-butyl-cyclopentadienyl)zirconium dimethyl, bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl, bis(n-octyl-cyclopentadienyl)zirconium dimethyl, and haloalkyl and dihalide complexes of the above; di-alkyl, trialkyl, tetra-alkyl, and penta-alkyl cyclopentadienes, such as bis(pentamethylcyclopentadienyl) zirconium di-methyl, bis(1,2-dimethylcyclopentadienyl)zirconium dimethyl and dihalide complexes of the above; silicone, phosphorus, and carbon bridged cyclopentadiene complexes such as dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide, and methylene dicyclopentadienyl zirconium dimethyl or dihalide, and methylene dicyclopentadienyl zirconium dimethyl or dihalide, carbenes represented by the formula $Cp_2Zr{=}CHP(C_6H_5)_2CH_3$, and derivatives of these compounds such as $Cp_2\underline{ZrCH_2CH(CH_3)CH_2}$.

Bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)vanadium dichloride and the like are illustrative of other metallocenes.

Various inorganic oxide supports may be used for supported catalyst systems to prepare polymers of the present invention. The polymerizations are generally carried in the temperature range of about 0-160°C or even higher but this range is not meant to be

exclusive for preparing the polymers of the invention which may be prepared by any technique resulting in the structure set forth. Atmospheric, sub-atmospheric, or super-atmospheric pressure conditions may exist for the polymerization using the metallocene catalyst described above. It is generally preferred to use catalyst compositions at a concentration so as to provide from about 1 ppm to about 5000 ppm, most preferably 10 ppm to 300 ppm, by weight of transition metal based on the weight of monomers in the polymerization of the ethylene polymers.

A slurry polymerization process may generally use sub-atmospheric or super-atmospheric pressures and temperatures in the range of 40-110°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The liquid employed in the polymerization medium can be alkane or cycloalkane, or an aromatic hydrocarbon such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of polymerization and relatively inert. Preferably, hexane or toluene is employed.

In a modification, polymers of the present invention may be formed by gas-phase polymerization. A gas-phase process utilizes super-atmospheric pressure and temperatures in the range of about 50°-120°C. Gas-phase polymerization can be performed in a stirred or fluidized bed of catalyst and product particles in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Thermostated ethylene, comonomer (including diene), hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at a temperature of 50°-120°C. Triethylaluminum may be added as needed as a scavenger of water, oxygen, and other adventitious impurities. Polymer product can be withdrawn continuously or semi-continuing at a rate such as to maintain a constant product inventory in the reactor. After polymerization and deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase reactor, freed of residual monomer with a nitrogen purge, and used without further deactivation or catalyst removal. The polymer obtained can

2008年5月29日 18時52分 発信電話番号 NO. 5624 P. 44

be extruded into water and cut into pellets or other suitable comminuted shapes. Pigments, antioxidants and other additives, as is known in the art, may be added to the polymer.

The molecular weight of polymer product obtained in accordance with this invention can vary over a wide range, as low as 500 up to 2,000,000 or higher and preferably 1,000 to about 500,000.

For the production of polymer product having a narrow molecular weight distribution, it is preferable to deposit only one metallocene on to the inert porous support material and employ said support metallocene together with the alumoxane as the polymerization catalyst.

It is highly desirable to have for many applications, such as extrusion and molding processes, polyethylenes which have a broad molecular weight distribution of the unimodal and/or the multimodal type. Such polyethylenes evidence excellent processability, i.e. they can be processed at a faster throughput rate with lower energy requirements and at the same time such polymers would evidence reduced melt flow perturbations. Such polyethylenes can be obtained by providing a catalyst component comprising at least two different metallocenes, each having different propagation and termination rate constants for ethylene polymerizations. Such rate constants are readily determined by one of ordinary skill in the art.

The molar ratio of the metallocenes, such as, for example, of a zirconocene to a titanocene in such catalysts, can vary over a wide range, and in accordance with this invention, the only limitation on the molar ratios is the breadth of the Mw distribution or the degree of bimodality desired in the product polymer. Desirably, the metallocene to metallocene molar ratio will be about 1:100 to about 100:1, and preferably 1:10 to about 10:1.

Examples

In the Examples following the alumoxane employed was prepared by adding 76.5 grams ferrous sulfate heptahydrate in 4 equally spaced increments over a 2 hour period to a rapidly stirred 2 liter round-bottom flask containing 1 liter of a 13.1 weight percent solution of trimethylaluminum (TMA) in toluene. The flask was maintained at 50°C and under a nitrogen atmosphere. Methane produced was continuously vented. Upon completion of the addition of ferrous

2008年5月29日 18時52分 欧州特許庁 NO. 5624 P. 45

sulfate heptahydrate, the flask was continuously stirred and maintained at a temperature of 50°C for 6 hours. The reaction mixture was cooled to room temperature and was allowed to settle. The clear solution containing the alumoxane was separated by decantation from the insoluble solids.

Molecular weights were determined on a Water's Associates Model No. 150C GPC (Gel Permeation Chromatography). The measurements were obtained by dissolving polymer samples in hot trichlorobenzene and filtered. The GPC runs are performed at 145°C in trichlorobenzene at 1.0 ml/min flow using styragel columns from Perkin Elmer, Inc. 0.1 percent solutions (300 microliters of trichlorobenzene solution) were injected and the samples were run in duplicate. The integration parameters were obtained with a Hewlett-Packard Data Module.

Example 1

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 500 cc of dry, degassed hexane directly into the pressure vessel 100 cc of purified 1,4-hexadiene was then charged into vessel with a gas tight syringe. 10.0 cc of 0.785 molar (in total aluminum) methyl alumoxane was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 60°C for 5 minutes at 0 psig of nitrogen. Bis(n-butyl-cyclopentadienyl)zirconium dichloride (1 mg) dissolved in 1.0 ml of dry, distilled toluene was injected through the septum inlet into the vessel. After 1 minute, ethylene at 60 psig was admitted and while the reaction vessel was maintained at 60°C. The ethylene was passed into the vessel for 10 minutes at which time the reaction was stopped by rapidly venting and cooling. 24.5 gms of ethylene/hexadiene copolymer was recovered after evaporation of the liquid component under nitrogen.

Example 1A

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry

2008年 5月29日 18時53分 特許庁審査第一部 NO. 5624 P. 46

ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 500 cc of dry, degassed toluene and 100 cc of dry, degassed 1,4-hexadiene was injected directly into the pressure vessel. 10.0 cc of 0.785 molar (in total aluminum) methyl alumoxane solution in toluene was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 70°C for 5 minutes at 0 psig of nitrogen. Bis(n-butylcyclopentadienyl)zirconium dichloride (0.10 mg) dissolved in 1.0 ml of dry, distilled toluene was injected through the septum inlet into the vessel. After 1 minute, ethylene at 50 psig was admitted and while the reaction vessel was maintained at 70°C. The ethylene was passed into the vessel for 30 minutes at which time the reaction was stopped by rapidly venting and cooling. 9.6 gms of ethylene/1,4-hexadiene copolymer was recovered after evaporation of the liquid components under nitrogen.

Example 2

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 500 cc of dry, degassed toluene, 50 cc of purified 1-hexene, and 50 cc of dry, degassed 1,4-hexadiene were injected directly into the pressure vessel. 10.0 cc of 0.785 molar (in total aluminum) methyl alumoxane solution in toluene was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 70°C for 5 minutes at 0 psig of nitrogen. Bis(n-butyl-cyclopentadienyl)zirconium dichloride (0.10 mg) dissolved in 0.10 ml of dry, distilled toluene was injected through the septum inlet into the vessel. After 1 minute, ethylene at 50 psig was admitted and while the reaction vessel was maintained at 70°C. The ethylene was passed into the vessel for 30 minutes at which time the reaction was stopped by rapidly venting and cooling. 5.1 gms of ethylene-1-hexene-1,4-hexadiene terpolymer was recovered after evaporation of the liquid components under nitrogen.

Example 2A

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature

2008# 58298 18#538 新国際特許部 NO. 5624 P. 47

control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 500 cc of dry, degassed hexane was added directly into the pressure flow. 100 cc of purified 4-vinylcyclohexene was charged into reaction vessel with a gas tight syringe. 10.0 cc of 0.785 molar (in total aluminum) methyl alumoxane solution in toluene was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 70°C for 5 minutes at 0 psig of nitrogen.
Bis(n-butyl-cyclopentadienyl)zirconium dichloride (0.1 mg) dissolved in 1.0 ml of dry, distilled toluene was injected through the septum inlet into the vessel. After 1 minute, ethylene at 62 psig was admitted and while the reaction vessel was maintained at 60°C. The ethylene was passed into the vessel for 10 minutes at which time the reaction was stopped by rapidly venting and cooling. 25.6 gms of ethylene/4-vinyl cyclohexene copolymer polyethylene was recovered after evaporation of the liquid components under nitrogen.

Example 2B

A 1-liter stainless steel pressure vessel, equipped with an incline blade stirrer, an external water jacket for temperature control, a septum inlet and vent line, and a regulated supply of dry ethylene and nitrogen, was dried and deoxygenated with a nitrogen flow. 250 cc of dry, degassed toluene and 200 cc of purified 4-vinylcyclohexene were injected directly into the pressure vessel. 10.0 cc of 0.785 molar (in total aluminum) methyl alumoxane in toluene solution in toluene was injected into the vessel by a gas tight syringe through the septum inlet and the mixture was stirred at 1,200 rpms and 70°C for 5 minutes at 0 psig of nitrogen.
Bis(n-butylcyclopentadienyl)zirconium dichloride (0.05 mg) dissolved in 0.050 ml of dry, distilled toluene was injected through the septum inlet into the vessel. After 1 minute, ethylene at 25 psig was admitted and while the reaction vessel was maintained at 70°C. The ethylene was passed into the vessel for 3 minutes at which time the reaction was stopped by rapidly venting and cooling. 7.3 gms of ethylene/4-vinylcyclohexene copolymer was recovered after evaporation of the liquid components under nitrogen.

The structural properties of the polymers of the Examples

2008年 5月29日 18時53分 特許庁審査官 NO. 5624 P. 48

are reflected in the drawing figures and reported in the following Table. Data on commercial polymers are reported in the Table and displayed in the drawing figures for comparison.

2008年 5月29日 18時53分 欧州国際特許庁 NO. 5624 P. 49

TABLE

RESIN	COMONOMER CONTENT (MOLE PERCENT) TYPE	AMOUNT	TYPE	AMOUNT	Mw (X 10^3)	Mw/Mn	COMPOSITION DISTRIBUTION	CLUSTER INDEX	MELTING BEHAVIOUR DISTRIBUTION	PEAK M.P. (°C)
EXAMPLE 1	1,4 HEXADIENE	2.3	-	-	70.5	1.75	NARROW	5.0	NARROW	111.9
EXAMPLE 2	1,4 HEXADIENE	2.0	HEXENE-1	1.9	62.6	1.80	-	-[1]	NARROW	101.0
EXAMPLE 2A	4-VINYLCYCLO-HEXENE	0.4	-	-	95.3	1.87	NARROW	-	NARROW	120.5
3 - EXXON LL 3001	HEXENE-1	3.7	-	-	103.1	3.30	BROAD	12.1	BROAD	124.6
4 - DOWLOX 2045	OCTENE-1	2.8	-	-	114.6	3.67	BROAD	9.5	BROAD	124.3
5 - EXXON LL 1001	BUTENE-1	4.4	-	-	118.0	3.33	BROAD	11.7	BROAD	121.6
6 - DUPONT SCLAIR 110	BUTENE-1	3.3	-	-	115.7	3.79	BROAD	5.0	BROAD	118.7
7 - MITSUI 2020L	4-METHYL-PENTENE-1	3.5	-	-	92.3	2.6	BROAD	-	BROAD	124.5
8 - LLDPE[2]	BUTENE-1	5.2	-	-	96.1	1.78	NARROW	9.6	NARROW	94.0

1. ANALYZED BUT ONLY LOW QUALITY SPECTRA OBTAINED - IMPRECISE RESULT.

2. LABORATORY PREPARATION WITH A SOLUBLE VANADIUM OXYCHLORIDE/ETHYL ALUMINUM SESQUICHLORIDE CATALYST.

2008年 5月29日 18時54分 欧州特許庁

CLAIMS:

1. A copolymer composition from the polymerization of ethylene and at least one comonomer comprising an alpha, internal nonconjugated diene, said copolymer composition having incorporated in its structure at least 3 mole percent of units of said at least one comonomer, said copolymer composition having a cluster index of about 9 or less, and said copolymer composition having an alpha-olefin content less than 15 weight percent.

2. The copolymer composition of claim 1 having a molecular weight distribution of about 3.0 or less.

3. The copolymer composition of claim 2 having a molecular weight distribution of about 2.5 or less.

4. The copolymer composition of claim 3 having a molecular weight distribution of about 2.0.

5. The copolymer composition of claim 1 having a comonomer composition distribution wherein more than 55 weight percent of the copolymer is within 50 percent of the median comonomer content in mole percent, of said composition.

6. The copolymer composition of claim 5 having greater than 65 weight percent of the copolymers within 50 percent of the median comonomer content in mole percent.

7. A copolymer composition of claim 1 having a cluster index of about 7 or less.

8. A copolymer composition of claim 7 having a cluster index of about 5 or less.

9. The copolymer composition of claim 1 having a monomer composition comprising about 0.1-25 mole percent of said diene.

2008年 5月29日 18時54分 特許庁審査第四部 NO. 5624 P. 51

10. The copolymer composition of claim 9 having a monomer composition comprising about 0.1-10 mole percent of said diene.

11. The copolymer composition of claim 9 having a monomer composition comprising 0.1-2 mole percent of said diene.

12. The copolymer composition of claim 1 wherein said copolymer is an interpolymer comprising ethylene, said diene, and at least one other polymerizable unsaturated comonomer.

13. The copolymer composition of claim 1 wherein said at least one other polymerizable unsaturated comonomer is an alpha-olefin.

14. The copolymer composition of claim 1 wherein said alpha-olefin is propylene, butene-1, or hexene-1.

15. The copolymer composition of claim 1 having a density of about 0.85-1.0.

16. The copolymer composition of claim 15 having a density of about 0.87-0.90.

17. The copolymer composition of claim 15 having a density of about 0.90-0.915.

18. The copolymer composition of claim 15 having a density of about 0.915-0.940.

19. The copolymer composition of claim 15 having a density of about 0.940-0.960.

20. The copolymer composition of claim 2 having a comonomer composition distribution wherein greater than 55 weight percent of the copolymer is within 50 percent of the median comonomer content in mole percent.

2008年 5月29日 18時54分 特許庁審査第一部 NO. 5624 P. 52

21. The copolymer composition of claim 1 wherein said copolymer has incorporated in its structure at least 5 mole percent of units of said at least one comonomer.

22. The copolymer composition of claim 1 wherein said at least 5 mole percent units of said at least one comonomer includes at least about 0.01 mole percent of units of said diene.

23. The copolymer composition of claim 22 containing at least about 0.1 mole percent units of said diene.

24. The copolymer composition of claim 23 containing at least about 1 mole percent units of said diene.

25. The copolymer composition of claim 24 containing at least about 3 mole percent units of said diene.

26. The copolymer composition of claim 25 containing at least 5 mole percent units of said diene.

27. The copolymer composition of claim 1 wherein said at least 3 mole percent units of said at least one comonomer consist essentially of said diene.

28. The copolymer composition of claim 1 wherein said diene is a linear diene.

29. The copolymer composition of claim 28 wherein said linear diene is a 1,4-hexadiene, substituted or unsubstituted.

30. The copolymer composition of claim 29 wherein said diene is 1,4-hexadiene.

31. The copolymer composition of claim 1 wherein said diene is a cyclic diene.

32. The copolymer composition of claim 1 wherein said cyclic diene is 4-vinylcyclohexene.

33. The copolymer composition of claim 27 wherein said diene is 1,4-hexadiene.

34. A copolymer composition of ethylene and an alpha, internal nonconjugated diene (diolefin) having a cluster index of about 9 or less, a molecular weight distribution of about 3.0 or less, a comonomer composition distribution of more than 55 weight percent of the copolymer within 50 percent of the median comonomer content in mole percent, said copolymer being formed by polymerization in the presence of a catalyst system comprising a metallocene of a metal of Group IVB, VB, and VIB of the Periodic Table and an alumoxane or a reaction product thereof, and said copolymer composition having an alpha-olefin content less than 15 weight percent.

35. The copolymer composition of claim 34 wherein the catalyst system metallocene is represented by

$$(Cp)_mMR_nR'_p$$

wherein Cp is a substituted or unsubstituted cyclopentadienyl ring; M is a Group IVB, VB, or VIB transition metal; R and R'; are independently selected halogen, hydrocarbyl group, or hydrocarboxyl group having 1-20 carbon atoms; m = 1-3, n = 0-3, p = 0-3, and the sum of m + n + p equals the oxidation state of M.

2008年 5月29日 18時54分 欧州国際特許部 NO. 5624 P. 54

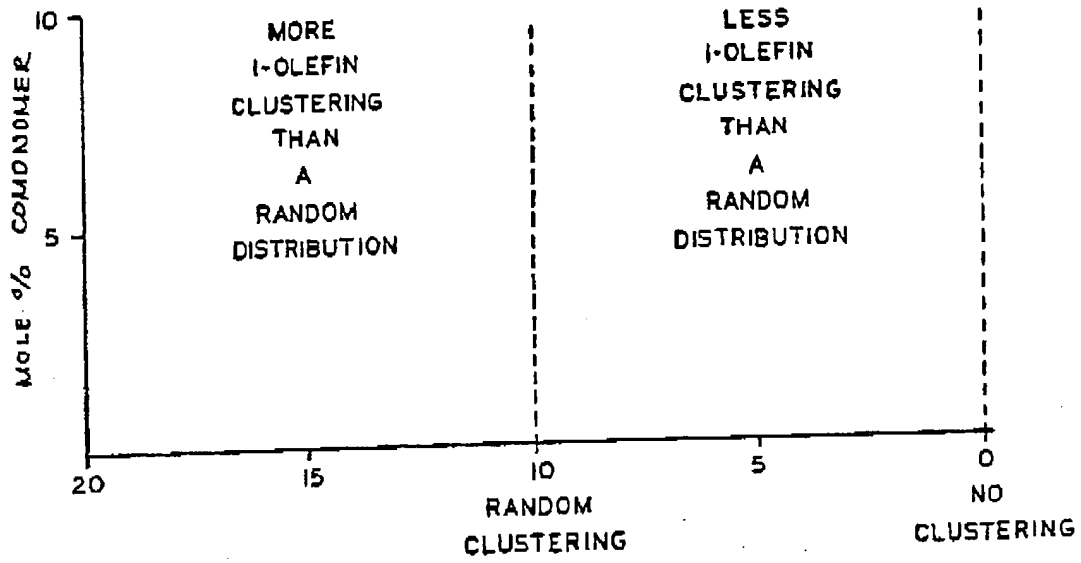

MORE
1-OLEFIN
CLUSTERING
THAN
A
RANDOM
DISTRIBUTION
LESS
1-OLEFIN
CLUSTERING
THAN
A
RANDOM
DISTRIBUTION
MOLE % COMONOMER
10
5
20
15
10
5
0
RANDOM
CLUSTERING
NO
CLUSTERING

FIG.1

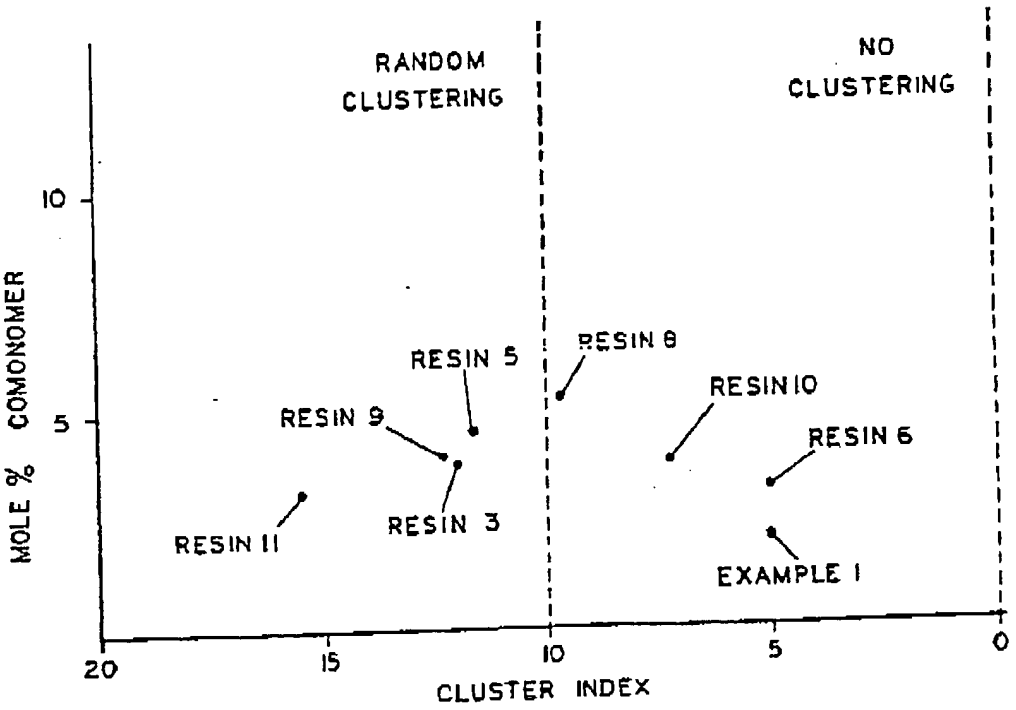

RANDOM
CLUSTERING
NO
CLUSTERING
MOLE % COMONOMER
10
5
RESIN 5
RESIN 8
RESIN 9
RESIN 10
RESIN 6
RESIN 3
RESIN 11
EXAMPLE 1
20
15
10
5
0
CLUSTER INDEX

FIG.2

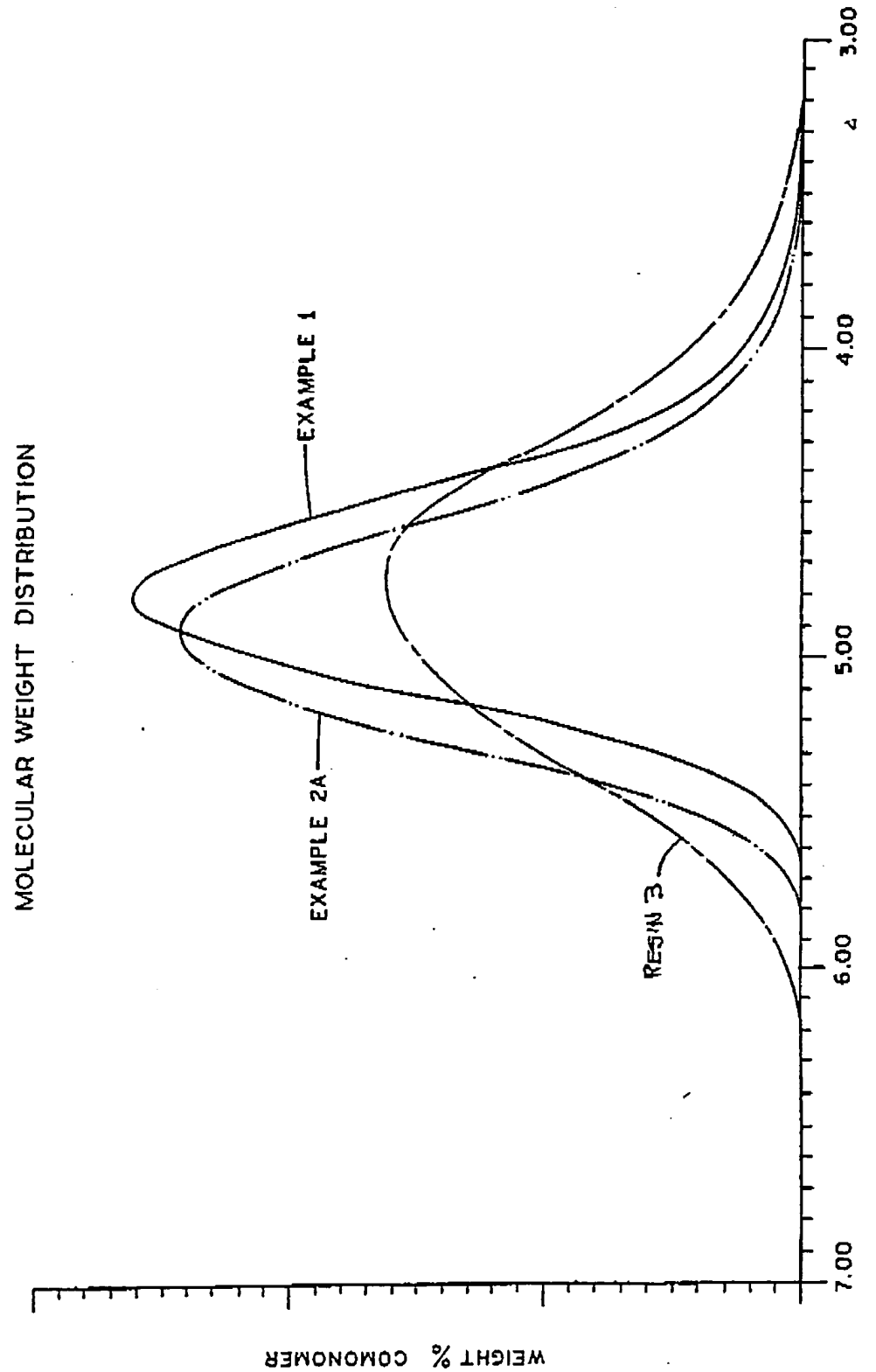

MOLECULAR WEIGHT DISTRIBUTION
EXAMPLE 1
EXAMPLE 2A
RESIN 3
WEIGHT % COMONOMER
3.00
4.00
5.00
6.00
7.00
LOG (MW)

FIG. 3

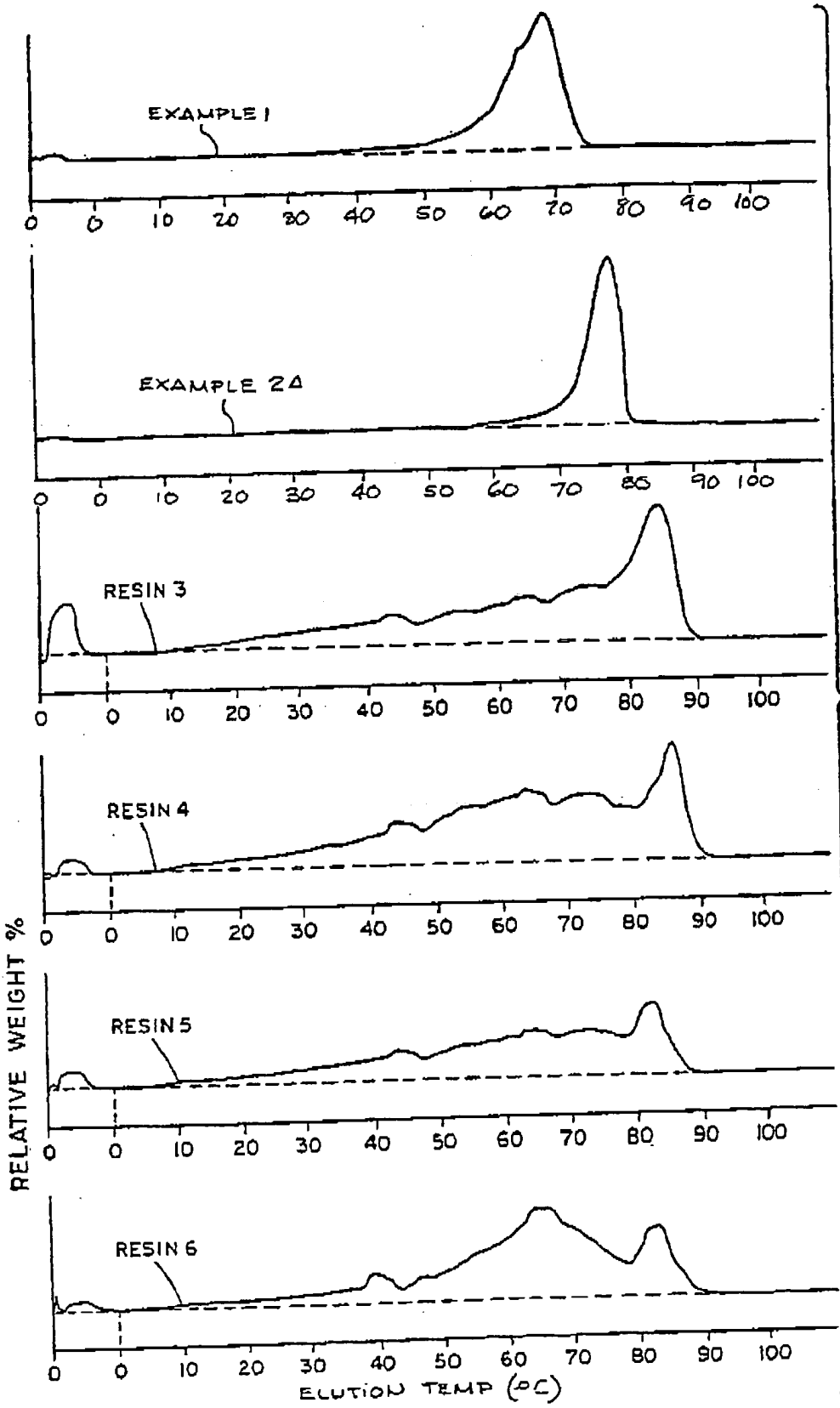
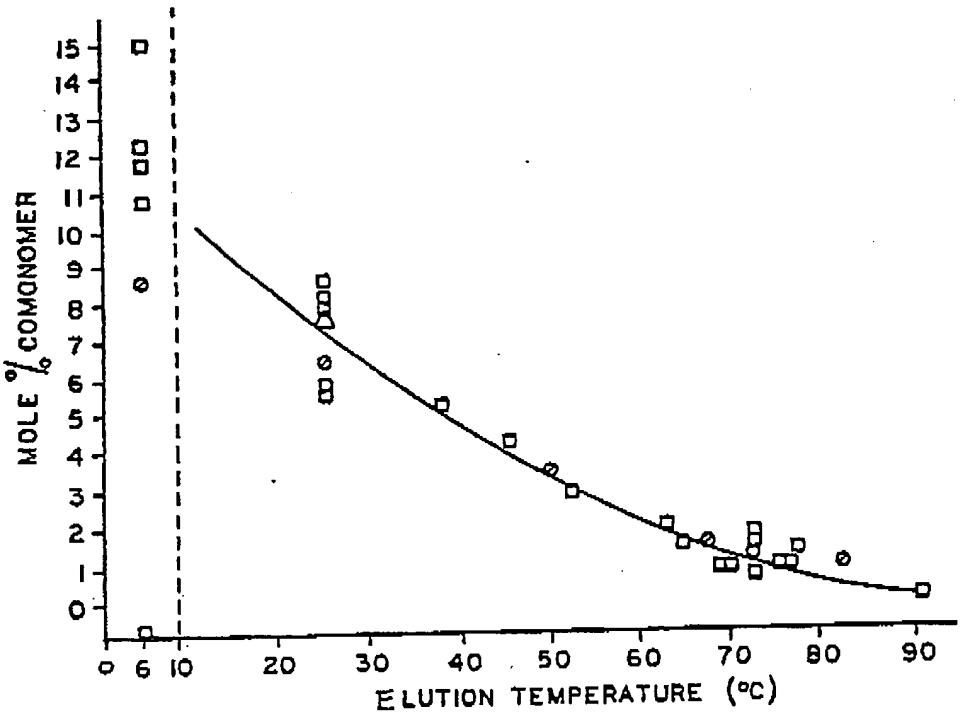

EXAMPLE 1
EXAMPLE 2A
RESIN 3
RESIN 4
RESIN 5
RESIN 6
RELATIVE WEIGHT %
ELUTION TEMP (°C)
0 0 10 20 30 40 50 60 70 80 90 100

FIG4



BUTENE COMONOMER	⊘
HEXENE COMONOMER	□
OCTENE COMONOMER	△

FIG.5

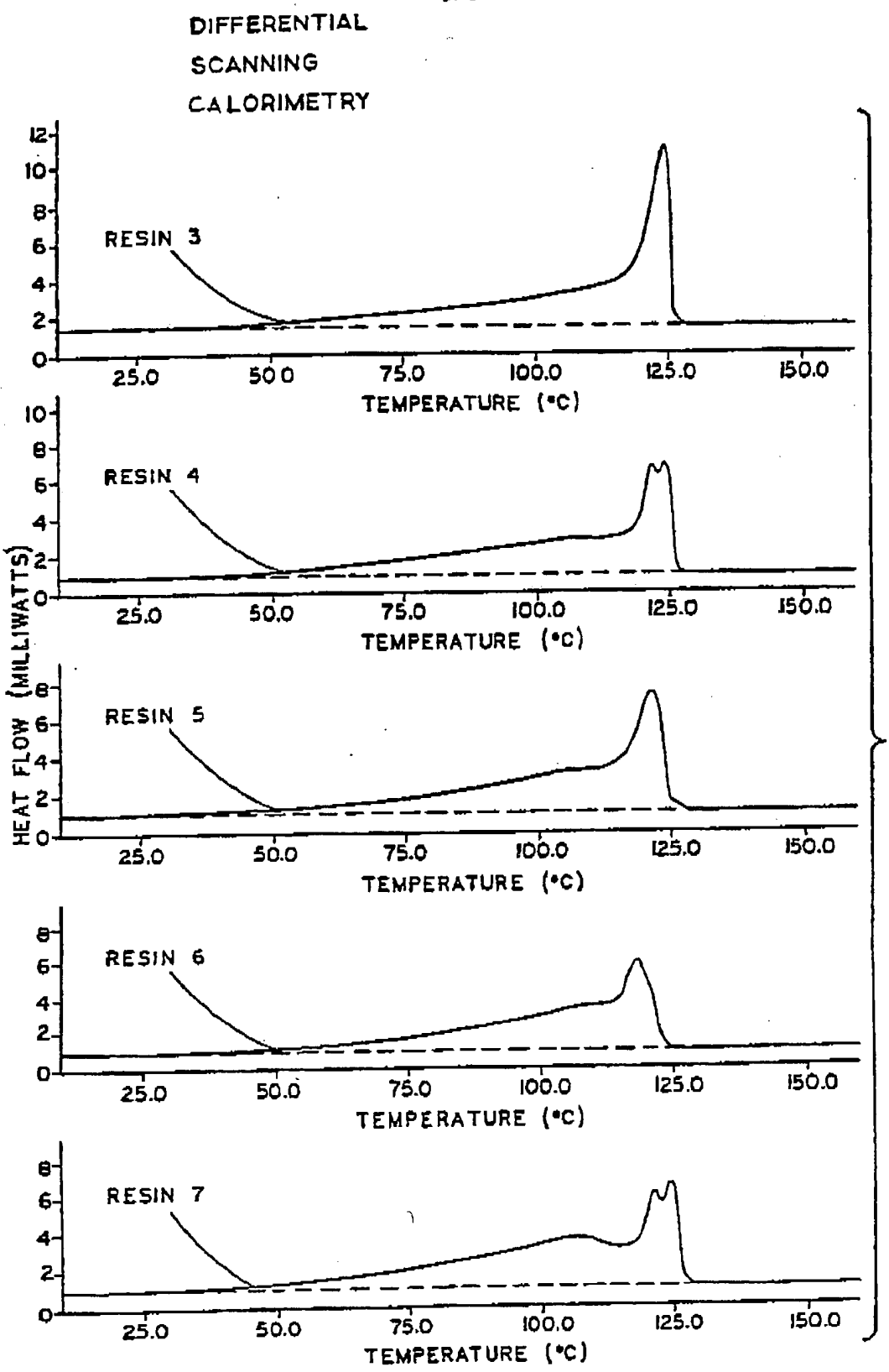

DIFFERENTIAL
SCANNING
CALORIMETRY
RESIN 3
RESIN 4
RESIN 5
RESIN 6
RESIN 7
HEAT FLOW (MILLIWATTS)
TEMPERATURE (°C)
25.0
50.0
75.0
100.0
125.0
150.0

FIG.6

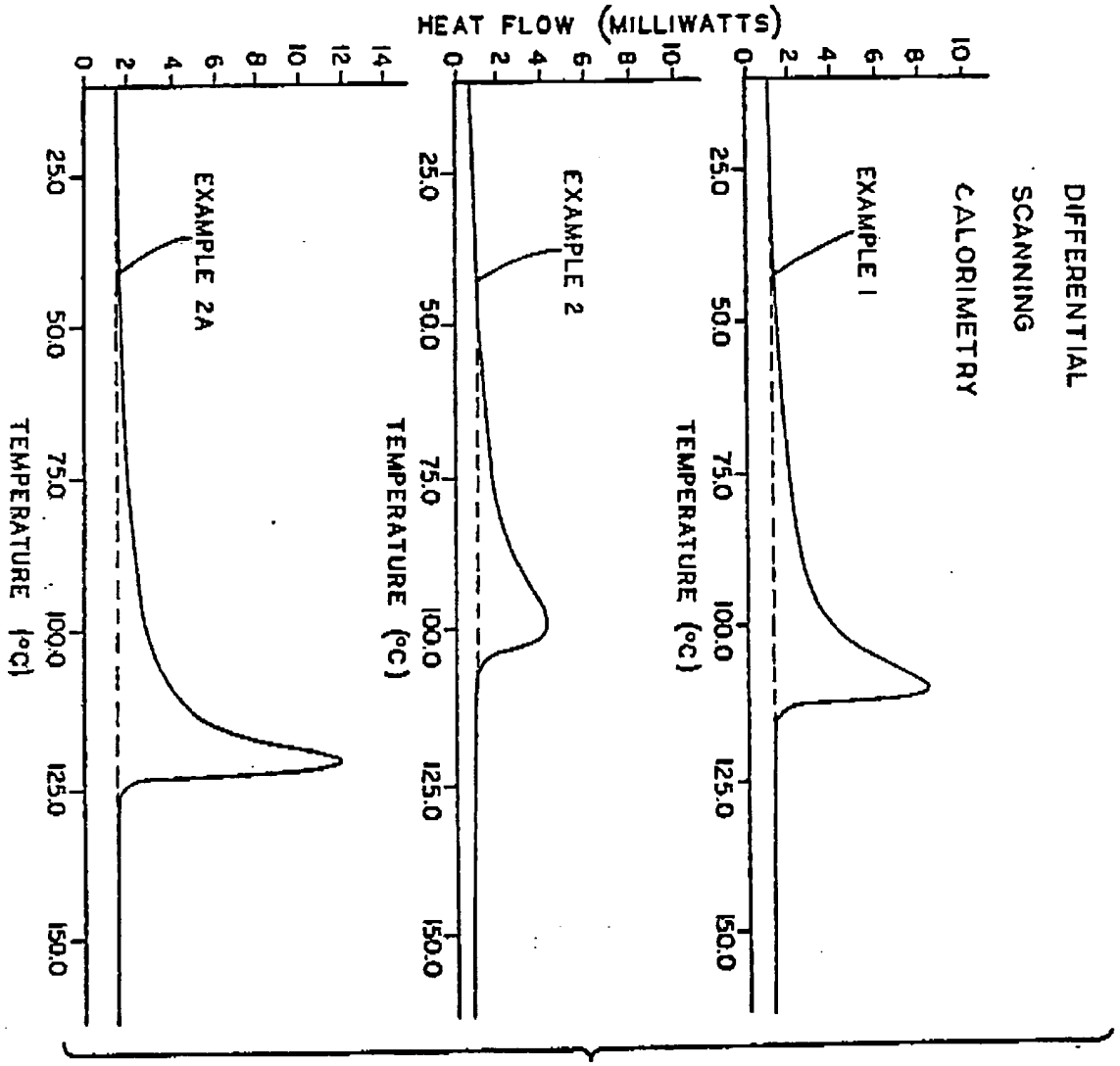

DIFFERENTIAL
SCANNING
CALORIMETRY
HEAT FLOW (MILLIWATTS)
EXAMPLE 1
EXAMPLE 2
EXAMPLE 2A
TEMPERATURE (°C)
25.0
50.0
75.0
100.0
125.0
150.0

FIG.6A

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/03299

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: C 08 F 210/18

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[4]	C 08 F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	EP, A, 0069951 (HOECHST) 19 January 1983 see claims 1-8 --	1
A	US, A, 4306041 (C. COZEWITH) 15 December 1981 see claims 1-19; column 3, lines 34-56 --	1
A	GB, A, 2099836 (MONTEDISON) 15 December 1982 see claims 1-7 --	1
P,X	EP, A, 0223394 (UNIROYAL CHEMICAL) 27 May 1987 see claims 1-17; page 3, line 42 - page 5, line 15	1-35

---

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
15th April 1988	02 JUN 1988
International Searching Authority: EUROPEAN PATENT OFFICE	Signature of Authorized Officer: P.C.G. VAN DER PUTTEN

Form PCT/ISA/210 (second sheet) (January 1985)

2008年 5月29日 18時55分 特許庁審査第一部 NO. 5624 P. 61

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 8703299 SA 20109

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 11/05/88 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A- 0069951	19-01-83	DE-A-	3127133	27-01-83
		JP-A-	58019309	04-02-83
		CA-A-	1190998	23-07-85
		US-A-	4542199	17-09-85
US-A- 4306041	15-12-81	None		
GB-A- 2099836	15-12-82	BE-A-	893443	08-12-82
		FR-A-	2507189	10-12-82
		JP-A-	58002310	07-01-83
		NL-A-	8202251	03-01-83
		DE-A-	3221853	17-02-83
EP-A- 0223394	27-05-87	AU-A-	6397686	30-04-87
		JP-A-	62095304	01-05-87
		US-A-	4668834	26-05-87

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

2008年 5月29日 18時56分 特許庁審査部 NO. 5624 P. 62